

PROGRESS REPORT

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The purpose of this research is to search for a measure of order which can be applied to the evolution that can take place in a pre-biological system. First we shall look at generalizations that can be made and finally we plan an application to a specific chemical model system.

The first measure of order that appeared to be interesting was the energy of electronic ^{excitation}. Consider the simplest possible chemical system, a box of rare gas atoms such that the internal energy of the atoms is different than for the equilibrium state. This might be caused by some method of optical pumping. We have a state where the number, N_i , is in the i^{th} state whose energy is E_{ai} . The total internal or electronic energy, E_{int} , is:

$$E_{\text{int}} = \sum N_i E_{ai} \quad (1)$$

We now isolate the system adiabatically and the population of the i^{th} state changes to N_i (eq.) which is determined by the final temperature. The final internal energy is:

$$E_{\text{int}} = \sum N_i (\text{eq.}) E_{ai} \quad (2)$$

By defining the problem the way we did (i.e. atoms are in ^{excited} states)

$$E_{\text{int}} > E_{\text{int}}^{\text{I}}$$

The difference $E_{\text{int}} - E_{\text{int}}^{\text{I}}$ must go into the translational energy of the atoms, K_a . The final translational energy is K_a^{I} which is larger than K_a . We are assuming no interaction between the atoms except possibly for collections of the second kind when internal energy becomes translational. Thus the kinetic energy of the atoms increases.

What about the kinetic energy of the electrons in the atoms? Since the electrons kinetic energy is not quantized we shall use the quantum mechanical

virial theorem (1):

$$\bar{K}_{ei} = - E_{ai} \quad (3)$$

Initially $\bar{K}_e = \sum N_i K_{ei} = - E_{int}$

Finally $\bar{K}_e' = \sum N_i(e.q.) \bar{K}_{ei} = - E_{int}'$

The increase in K_e is $E_{int} - E_{int}'$ which is positive and as much as the increase in kinetic energy of the atoms.

The most important result is that kinetic energy of the atoms increases upon isolation, coming from the energy of electronic exatation. This result is due to two physical principles. (1) Conservatition of energy and (2) the density of translational states is very high compared to electronic states.

Next we consider a collection of interacting atoms which we assume has been exated to some higher electronic state. We will isolate the system and allow it to come to equilibrium. The total energy of the collection E is the sum of E_e , electronic energy, the kinetic energy of the nuclei K_n and the potential energy of interaction, ϕ of the nuclei. If there is a loss in electronic energy E_e then this must finally appear in the energy of the nuclei. Thus:

$$-\Delta E_e = \Delta K_n + \Delta \phi > 0 \quad (4)$$

Now according to the Born-Oppenheimer approximation the potential energy as a function of nuclear position is the electronic energy E_e . The transition takes place without a change in nuclear coordinates and

$$-\Delta E_e = \Delta K_n > 0 \quad (5)$$

The change in the kinetic energy of the nuclei is positive. If the system is then allowed to come to equilibrium the nuclear coordinates will vary with time.

Taking the time average

$$\Delta \bar{K}_n > 0 = 2 \Delta \bar{E}_e \quad (6)$$

The kinetic energy of the nuclei must increase upon isolation of the system and is a measure of the electronic exatation. If the electronic exatation is

a measure of the energy of a living system then by finding the increase of nuclear kinetic energy during adiabatic isolation, we shall be finding an interesting quantity.

As a special case of these general considerations we are investigating the change in the kinetic energy of the atoms upon isolation of a simple chemical system. The system whose chemical kinetics has been studied extensively is:



We are considering a volume separated by a Knudsen barrier to allow for matter flow and energy transport. One side of the barrier is at temperature T . The other side is at temperature $T + \Delta T$. We shall try to analyze this model to study the above general considerations.

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- (1) J.O. Hirschfelder, C.F. Curtiss and R. B. Bird, "Molecular Theory of Gases and Liquids." Wiley, New York. Page 68.
 - (2) J.O. Hirschfelder, C.F. Curtiss and R.B. Bird, "Molecular Theory of Gases and Liquids." Wiley, New York.
 - (3) J.O. Hirschfelder, Zeitschrift fur Physikalische Chemie Neue Folge, 37, 3/4, 1963.